Attosecond spectroscopy of solids: streaking phase shift due to lattice scattering

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Theory of laser-assisted photoemission from solids is developed for a numerically exactly solvable model with full inclusion of band structure effects. The strong lattice scattering in the vicinity of band gaps leads to a distortion and a temporal shift of the streaking spectrogram of the order of 100 as. The effect is explained in terms of Bloch electron dynamics and is shown to remain large for an arbitrarily small photoelectron mean free path. The implications for the streaking experiment on W(110) [A. L. Cavalieri *et al.*, Nature (London) **449**, 1029 (2007)] are discussed.

Attosecond photoelectron streaking is a unique tool to study ultrafast electronic processes with subfemtosecond resolution [1]. The method relies on mapping time to energy by means of a strong laser field: the electron wave packet created by an ultrashort pulse of extreme ultraviolet radiation (XUV) is accelerated by the superimposed laser field, and its energy spectrum $J(\epsilon)$ shifts up or down depending on the momentum transfer from the laser field to the outgoing electron. The energy gain depends on the electron release time τ relative to the laser field $E_{\mathrm{L}}(t)$, as encoded in the spectrogram $J(\epsilon, \tau)$. In comparison to the isolated atom, the application of the method to solids is complicated by two factors. First, the outgoing wave is a coherent superposition of contributions from many atoms. Second, the crystal lattice strongly affects the propagation of the photoelectron.

In the seminal experiment on W(110) by Cavalieri *et al.* [2] a shift of $\Delta\tau = 110 \pm 70$ as was discovered between the spectrograms of valence $5d$ and semi-core $4f$ states. Its origin has been debated in recent theoretical studies [3–6]. In Refs. [3–5] the original idea [2] is developed that the shift is due to a spatial inhomogeneity of the streaking field: under the assumption that the laser field does not penetrate into the crystal the measured $\Delta\tau$ is just the difference in the travel time to the surface for $5d$ and $4f$ electrons. Baggesen and Madsen [3] proposed to use the states located outside the metal as a reference to measure the absolute travel times. In the classical simulation by Lemell *et al.* [4] the streaking phase shift was traced back to the escape depth and to the electron group velocity. Kazansky and Echenique [5], however, questioned the applicability of the concept of group velocity as derived from band structure and ascribed the delay both to the different character of the initial $5d$ and $4f$ states and to a different propagation of the outgoing electrons. Contrary to the other authors, Zhang and Thumm [6] assumed the laser field to be spatially constant up to the escape depth of 5 Å, but, similar to Ref. [5], found the difference in the localization of the initial states to be the reason for their different streaking behavior. One important aspect not considered in previous studies is the Bloch nature of the outgoing electron and its implications for the streaking spectrogram.

Knowledge of the crystal lattice scattering effects is essential for the understanding of what is being measured in a streaking experiment on a solid. The aim of the present Letter is to shed light on how the band structure affects the formation of the spectrogram. Its role is twofold: First, close to the band gaps, the group velocity of the outgoing electron is reduced, which reduces the energy transfer to the photoelectron even if the laser field in the solid is as strong as in vacuum. Second, if the final state is close to a band gap edge, an electron at the surface is brought by the XUV pump pulse towards the crystal interior before it goes back and leaves the solid. This complicated trajectory causes a distortion of the spectrogram, which can be perceived as a final-state-energy dependent delay in photoemission. The joint effect of the two factors is shown to result in values of $\Delta\tau$ of the order of 100 as, i.e., close to those experimentally observed.

To arrive at reliable conclusions on the dependence of $\Delta\tau$ on the final state energy it is necessary to avoid any uncontrollable numerical approximations. We consider a model crystal surface without lateral corrugation, for which the time-dependent Schrödinger equation (TDSE) can be solved and the spectrogram $J(\epsilon, \tau)$ can be obtained with any desired accuracy. The periodic lattice is represented by a slab of 24 atomic layers with a piecewise constant potential $V(z)$, see Fig. 1(a). We consider normal emission and assume a linear polarization of the light with electric field along the surface normal, so the problem reduces to a one-dimensional (1D) TDSE. The perturbing field $E(t)$ is a superposition of an XUV and a laser pulse, see Fig. 1(c). The temporal envelopes of both pulses are of the form $\cos^2(\pi t/D)$. The full duration of the XUV pulse is $D = 500$ as. The laser pulse is chosen to be an odd function of t: $E_{\mathrm{L}}(t) = E_{\mathrm{L}}^{\mathrm{M}} \sin(\Omega t) \cos^2(\pi t/D)$, with photon energy $\Omega = 1.65$ eV, $D = 5$ fs, and amplitude $E_{\mathrm{L}}^{\mathrm{M}} = 2 \times 10^7$ V/cm. The system is enclosed in a box [Fig. 1(b)], and all calculations are performed in matrix form in terms of exact eigenfunctions (discrete spectrum) of the unperturbed Hamiltonian $\hat{H} = \hat{p}^2/2m + V(z)$. The
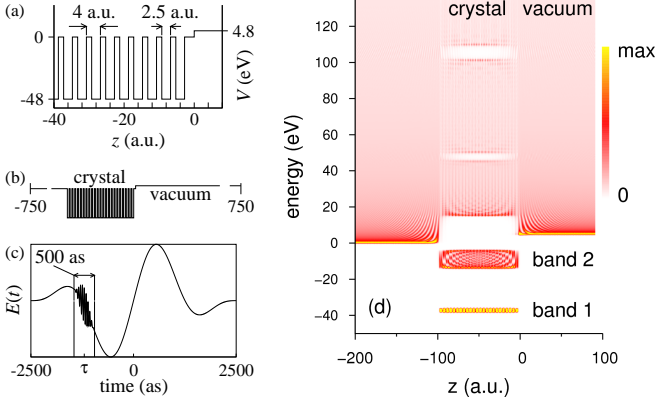
FIG. 1: (color online) (a) Potential profile of the model crystal. Atomic layers are given by potential wells, lattice constant is 4 a.u. (b) Domain of $\hat{H}$: $-750 \leq z \leq 750$ a.u. (c) Sum of XUV and laser pulses. (d) z-resolved density of states (DOS). Energy is relative to the "muffin-tin" (MT) zero.

electric field perturbation is taken in the dipole approximation, $\Delta\hat{H} = zeE(t)$. Note that the XUV pulse is not separated from the laser pulse – input into $\Delta\hat{H}$ is their sum. The TDSE is solved with the split-operator technique in the spectral representation, so the effect of the crystal potential is fully taken into account for both initial and final states. The spectrum of $\hat{H}$ is truncated at 200 eV above the vacuum level, which ensures the convergence of all the results. More details of the methodology can be found in Ref. [7], where the model was applied to a single atom.

Initial states are the two bound bands, see Fig. 1(d): the narrow band (1) and the wide band (2), respectively, model semi-core and valence states. Each initial state gives rise to two wave packets traveling in opposite directions. When both pulses are over and the right-traveling packet has left the crystal, it is reexpanded in terms of the eigenfunctions of $\hat{H}$ to yield the recorded spectrum. The observed spectrum $J(\epsilon, \tau)$ is a sum of the spectra of the 24 levels representing the band. The centroid (center of gravity) of the total streaked spectrum $\tilde{\epsilon}(\tau)$ shifts relative to the centroid of the laser-free spectrum $\tilde{\epsilon}_0$, and the dependence of the shift on the release time τ is referred to as the streaking curve, $s(\tau) = \tilde{\epsilon}(\tau) - \tilde{\epsilon}_0$. Note that for a classical particle created at the time τ and moving under the field $E_L(t)$ in a flat potential $V(z) = \mathrm{const}$, the streaking curve is symmetric: $s(\tau) = s(-\tau)$.

Let us start with the obvious observation that the average potential in the crystal U is lower than the potential in vacuum, so in the crystal a classical electron moves faster than in vacuum. Thereby its streaking curve deviates from that of a free particle, and this distortion can be perceived as a delay of the release of the photoelectron coming from the depth of the crystal relative to the one released just at the surface. For example, in the present case, the momentum transfer for a free electron would be

maximal at $\tau = 0$, but because at that point the electric field increases the electron in the crystal gains more energy if it starts later to be exposed to a stronger field while it moves faster. Figure 2(a) shows the exact result for a classical particle (full line) starting from the depth of 55 a.u. with the initial kinetic energy of 94 eV in a solid with an inner potential of $U = -30$ eV. This corresponds to the excitation of the narrow band by the XUV pulse of $\omega = 106$ eV ($\epsilon = 69$ eV), and the fully quantum-mechanical calculation yields an almost identical streaking curve: it is seen to be shifted to the right by ~ 50 as from the free-particle curve [8]. What happens when the final state is close to a band gap, where the electron group velocity in the crystal is lower than in vacuum? Here, by the Bloch electron dynamics law $\hbar dk/dt = F$, its energy changes slower than in vacuum, and the opposite effect is expected. Indeed, for $\omega = 155$ eV ($\epsilon = 118$ eV) the $s(\tau)$ curve is shifted to the left, see Fig. 2(b), i.e., the electron appears to be released earlier than the free particle.
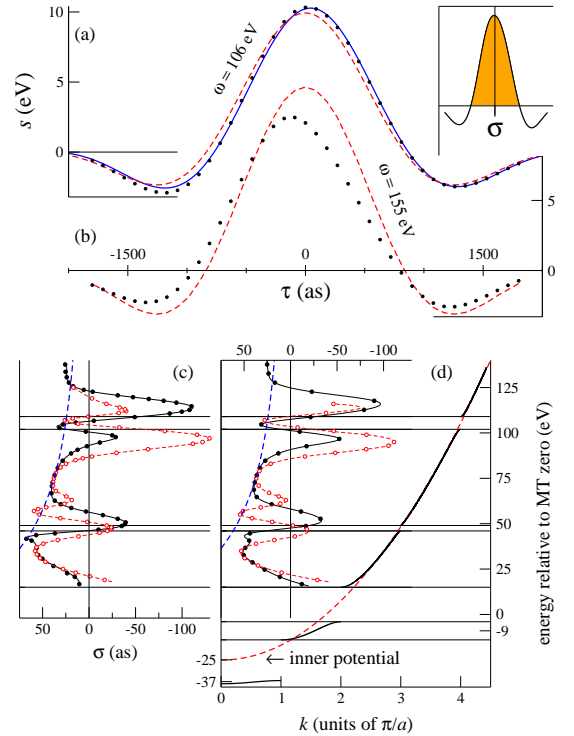

FIG. 2: (color online) (a) Blue solid line is for a classical particle traversing the potential barrier U. (a) and (b) Circles are the $s(\tau)$ values by TDSE for the emission from band 1 ($\epsilon_{\mathrm{ini}} = -37$ eV) with $\omega = 106$ eV (a) and 155 eV (b). Red dashed lines are for a classical particle (starting with the same kinetic energy) in a flat potential. Inset illustrates the definition of σ. (c) and (d) Streaking curve shift $\sigma(\epsilon)$ for a classical particle (thick dashed line) and for emission from band 1 (black full circles) and band 2 ($\epsilon_{\mathrm{ini}} = -9 \pm 5$ eV, red open circles). $\epsilon = \epsilon_{\mathrm{ini}} + \omega$. Laser field is $E_L^M = 2 \times 10^7$ V/cm (c) and 4×10^7 V/cm (d). Shown to the right are the crystal band structure $\epsilon(k)$ and the parabolic fit to the unbound spectrum (red dashed line) to determine the inner potential U.

For the special case of an odd function $E_L(t)$ the temporal shift of the curve can be roughly quantified as the center of gravity σ of the positive part of the function $s(\tau)$. Its dependence on the final energy $\sigma(\epsilon)$ for the classical particle and for both bands is shown in Figs. 2(c) and 2(d). Far from the band gaps the streaking curve shows a delay, and σ is close to that for a classical particle starting at -55 a.u., which is slightly deeper than the average spatial location of the initial states, -48 a.u. When the final state energy approaches a band gap the $s(\tau)$ curve strongly deviates from the free-electron shape, and the function $\sigma(\epsilon)$ shows oscillations. This is caused by rapid energy variations of the photoemission cross-section in combination with the large energy width of the pump pulse [9], so that the spectrum is composed of several contributions, which are differently streaked by the probe field. Nevertheless, when the spectral weight concentrates close to a band-gap edge, the $s(\tau)$ curve retains an approximately symmetric shape and shifts to the left, showing an advance (negative σ). The $\sigma(\epsilon)$ curves are rather stable to the strength of the streaking field: a two times larger amplitude E_L^M yields almost the same result [cf. Figs. 2(c) and 2(d)]. This proves the robustness of the effect and that the parameter σ is a reasonable choice to characterize its range. The $\sigma(\epsilon)$ curves are very similar for the emission from the narrow and from the wide band, with more oscillations in the latter case due to the much broader spectrum of the wide band. Far from the gaps the values of σ for the two bands closely agree, demonstrating the dominant role of final states.

We may conclude that the semi-classical picture based on the notions of inner potential and group velocity is a good starting point to understand the τ-shift of the streaking curve. To relate it to the experiment, we must take into account the surface sensitivity of photoemission: owing to inelastic scattering, only the electrons excited in a close vicinity of the surface contribute to the observed spectrum. The travel path to leave the crystal is, thus, limited by the escape depth λ, and for sufficiently small λ the effect of *delay* that occurs in nearly-free-electron (NFE) regions (far from band gaps) must become negligible. However, the effect of *advance* would not completely disappear even for a small λ of few Angstroms because close to the gap the velocity may be arbitrarily small. For an unambiguous analysis of the escape depth effect it is desirable to avoid a phenomenological treatment of inelastic effects by an imaginary absorbing potential and current non-conservation. To introduce a spatial resolution into the microscopic theory, let us create a defect in the 1D lattice and study the streaking of the photoelectron from the localized state at the defect.

Figure 3 shows the energy dependent distortion of the streaking curves for the initial state localized at the defect in the first, second, and fourth layer. In accord with the above discussion, the effect of delay in the NFE regions is rather small (although it increases with the depth). How-
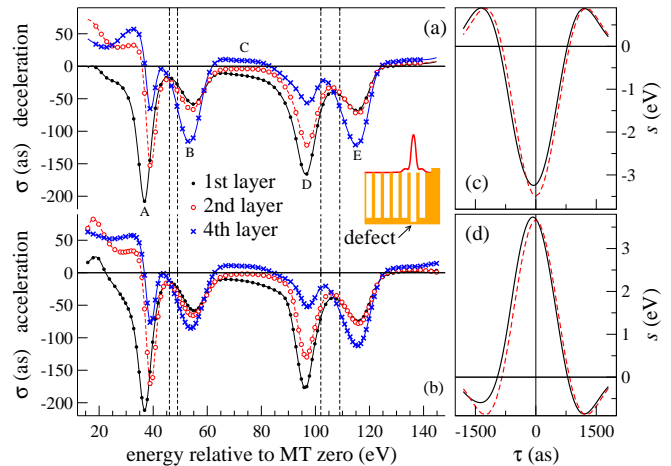

FIG. 3: (color online) (a) and (b) Delay $\sigma(\epsilon)$ for emission from the state at the defect (inset) in the 1st (black full circles), 2nd (red open circles), and 4th layer (blue crosses). $\epsilon_{\mathrm{ini}} = -41$ eV, $\epsilon = \epsilon_{\mathrm{ini}} + \omega$. (c) and (d) $s(\tau)$ for $\omega = 82$ eV for the defect in the 1st layer (full lines) and for a classical particle in a flat potential (dashed lines). Vertical lines show band gaps. (a) and (c) are for the laser pulse $E_L(t)$; (b) and (d) for $-E_L(t)$.

ever, the effect of advance is quite large: as in the case of the extended states, the variations of σ are comparable to the measured $\Delta\tau$ value. The most surprising is that for the 1st layer σ does not vanish – it is of the same order or even larger than for the 2nd and the 4th layer. Although for the electron released at the 1st layer there seems to be no space to traverse to leave the crystal, it appears to have spent some time in the crystal. In fact, the wave packet is brought inside the crystal by the pump pulse. This happens when the final state is at a band-gap edge, where the local DOS is larger in the crystal than in vacuum, see Fig. 1(d). Owing to the DOS gradient, the wave packet is shifted beneath the surface. Comparison of the streaking by the pulse in Fig 1(c) and by the pulse of the opposite sign (acceleration at $\tau = 0$ vs. deceleration) again indicates that the effect is a property of the system rather than of the specific perturbation.

Some features of the $\sigma(\epsilon)$ curves can be readily understood within the classical picture: the minima B and E and the maximum C are more pronounced for the deeper defects. The minima A and D, however, show the opposite trend. This happens when a rapid energy dependence of the photoemission cross-section leads to oscillations of σ. Close to the surface this energy dependence varies with the position of the defect, and at certain energies the effect becomes stronger for the 1st layer than for the deeper layers. Nevertheless, also in this case the streaking curves retain their traditional shape; an example for the topmost layer is shown in Figs. 3(c) and 3(d).

These results show that the streaking phase shift may occur at arbitrarily small escape depths and without the interference between the layers (in the case of the defect
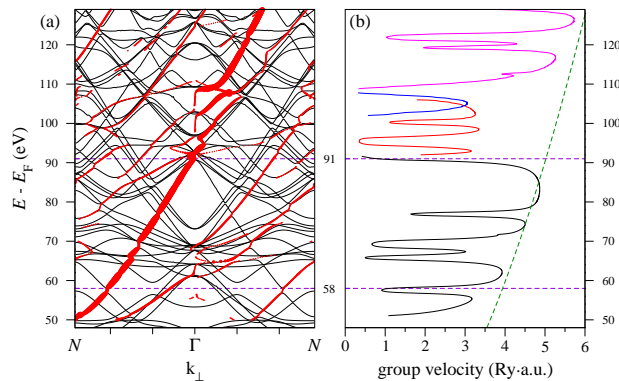
FIG. 4: (color online) (a) Real band structure (thin lines) and conducting complex band structure (red thick lines) of W(110). (b) Energy dependence of group velocity for four conducting branches (full lines) and in vacuum (dashed line).

it is explicitly excluded). This imposes a limitation on using the states located outside the metal as a zero-delay reference: the final states must be in an NFE region.

Finally, let us see whether the present theory is relevant to the experiment on tungsten. The band structure for the normal emission from the (110) surface ($N\Gamma N$ line) is shown in Fig. 4. To determine the Bloch waves that effect the electron escape into vacuum we draw on the one-step theory of photoemission, in which the final states are time reversed LEED states (low energy electron diffraction). The LEED wave functions are calculated from the complex band structure of the semi-infinite W(110) crystal with the linear augmented plane wave method as explained in Ref. [10]. The Bloch waves most strongly contributing to the LEED state – *the conducting branches* – are highlighted by the line thickness, which is proportional to the current carried by the individual partial wave (see Ref. [11] for the explanation). The energy dependence of the group velocity for the four conducting branches is shown in Fig. 4(b). The final states for photoemission from both $4f$ and $5d$ bands are seen to fall in the vicinity of the band gaps, at 58 and 91 eV, respectively. Thus, the effect of advance must occur in both cases, and, judging by the variations of σ given by the present model (as large as 150 as), it strongly contributes to the observed effect. Qualitatively, one may speculate that because the velocity mismatch is larger at higher energies the negative shift of the streaking curve should be larger for $5d$ than for $4f$ emission, which would give an advance of the $5d$ emission, as in the experiment.

To summarize, the final states band structure causes a τ-shift of the spectrogram, and its sign depends on whether the photoelectron moves in the crystal faster or slower than in vacuum. For an electron coming from a large depth and moving faster than in vacuum the streaking curve shifts towards positive delays. In the present 1D model (consistent with realistic $\mathbf{k}_\parallel$ projected band structure) the delay is within 50 as. This effect is in ac-

cordance with classical dynamics. Naturally, it steadily decreases with decreasing escape depth. The quantum nature of the outgoing electron becomes important for final energies sufficiently close to a band gap, where it always moves slower than in vacuum. In that case the spectrogram shows an advance. The quantum effect is found to exceed 100 as even for electrons excited from the states localized at the surface. This reveals an aspect important for various electron spectroscopies: the outgoing electrons are sensitive to the substrate band structure no matter how small the electron mean free path is.

The main implication for the attosecond spectroscopy is that neither the inhomogeneity of the streaking field nor an extended initial state are a prerequisite for an appreciable relative delay. Still, the mean free path plays a large role because depending on its value different aspects of the mechanism become important. Experimentally, the predicted effect should manifest itself as a non-monotonic dependence of $\Delta\tau$ on the XUV energy, and it must be allowed for in interpreting spectrograms. At the same time, measurements at different ω would be instrumental in separating the final-states effect from the effect of initial state and of the screening of the laser field and providing information on the factors involved.

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